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(54) Title: OLIGOMERIC, HYDROXY-TERMINATED PHOSPHONATES

(57) Abstract: Epoxy resins that are suitable for forming epoxy laminates that meet a UL-94 rating of v-0 comprise a hydroxy-terminated oligomeric phosphonate comprising the repeating structure -OP(=O) (R)OArylene-, where R is alkyl, as a flame retardant.

OLIGOMERIC, HYDROXY-TERMINATED PHOSPHONATES

5 The reaction of a phosphonyl dichloride with a diol produces in most cases aliphatic phosphonic structures (1,) with the polymers are low melting and hydrophilic. Industrial interest has been concentrated on the polyphosphonates made from aromatic diols or aromatic
10 phosphonyl dichlorides. Early studies showed that high molecular weight polyesters can be attained with carefully purified reactants and precise stoichiometry.

 Because of the commercial availability of phenylphosphonyl dichloride (benzene phosphorus
15 oxydichloride, BPOD), much work has been done on this intermediate to make polymeric phosphonates, including flame-retardant additives for poly(ethylene terephthalate) (2), poly(phenylene oxide)-polystyrene blends (3), and other thermoplastics.

20 Polyphenylphosphonates can be made from hydroquinone or resorcinol (4-8), tetrabromobisphenol A (9), tetrabromobisphenol and sulfonylbisphenol (10), neopentylene glycol (11), 4,4'-dihydroxybiphenyl or 4,4'-bis(4-hydroxyphenyl)fluorene (12), and 2,2'-bis(bromomethyl)-1,3-
25 propanediol (13). Polymeric alkyl- and arylphosphonates of various bisphenols promote flame retardancy in polyacrylonitrile and nylon-6,6 (14). Copolycondensation products from resorcinol and phenylphosphonic dichloride and phenyl phosphorodichloridate are flame retardants for
30 thermoplastic polyesters (14, 15). Toyobo introduced such a

polymer in Japan for polyester fibers to meet the Japanese flame-retardant regulations for home furnishings (16, 17).

Interfacial polycondensations for the synthesis of polyphosphonates are very rapid and, under favorable
5 conditions, give high molecular weights (18).

Transesterification of a Phosphonate with a Diol: This method is complicated with O,O-dialkyl phosphonates by side reactions in which the phosphonate acts as an alkylating agent. However, with O,O-diaryl phosphonates, ester exchange
10 is an effective route to polymeric phosphonates (19-22):

Higher molecular weights can be attained by adding tri- or tetrahydric phenols or triaryl phosphates to the reaction mixture (23). A transparent poly(methylphosphonate) thermoplastic made by this technology was reported to be in
15 development at one time by Bayer for use in flame-retardant aircraft applications, as well as for windshields, goggles, and police riot-control shields (21, 24). Their mechanical properties are excellent, although resistance to hot water may be somewhat deficient (21). These polyphosphonates can
20 be mixed with polycarbonates to make flame-retardant polymer blends (22). By inclusion of diphenyl carbonate in the transesterification, copolycondensed polyphosphonate carbonates can be made (21,); these were possibly, at one time, in development for aerospace applications. By
25 transesterification of diphenyl methylphosphonate and diphenyl iso- and terephthalate with bisphenols, high molecular weight polyarylates with favorable properties as plastics were made (21).

The aryl-containing analogues to the hydroxy-terminated
30 oligomeric phosphonate additive, which is the subject matter

of the present invention, is known (25) but would be of lower phosphorus content than the additive contemplated herein.

The problems of brominated FR-containing epoxy encapsulants has been described (26). Epoxy resin compositions that are suitable for encapsulating (or sealing) a semiconductor have contained monomeric phosphoric acid ester flame retardants (27).

Finally, it is known to synthesize poly(m-phenylene methylphosphonate) by the transesterification of diphenyl methylphosphonate with resorcinol (28). However, such a product made in that manner contained phenyl end groups which would exclude reactivity of such a product with an epoxy polymer.

References:

1. U.S. Patent No. 2,891,915.
2. R. Stackman, Ind. Eng. Chem. Prod. Res. Dev. 21, 332 (1982).
3. Ger. Offen. DE 31 39 958 A1 (Apr. 28, 1983).
4. U.S. Patent No. 2,435,252.
5. U.S. Patent No. 2,716,101.
6. H. W. Coover et al., Ind. Eng. Chem. 52(5), 409 (1960).
7. Jpn. Kokai 72 39,154 (Dec. 6, 1972).
8. U.S. Patent No. 3,326,852.
9. U.S. Patent No. 3,932,351.
10. U.S. Patent No. 4,229,552.
11. U.S. Patent No. 4,033,927.
12. Y. Imai et al., J. Polym. Sci. Polym. Chem. Ed. 22(6), 1259 (1984).
13. U.S. Patent No. 3,925,303.
14. A. Natansohn, J. Appl. Polym. Sci. 32, 2961 (1986).
15. U.S. Patent Nos. 3,829,405 and 3,830,771.
16. U.S. Patent No. 3,719,727.
17. K. S. Kim, J. Appl. Polym. Sci. 28, 1119 (1983) and U.S. Patent No. 4,206,296.

18. C. E. Carraher, Jr., *Inorg. Macromol. Rev.* 1, 287 (1972).

19. U.S. Patent No. 2,682,522.

20. U.S. Patent No. 4,152,373.

5 21. M. Schmidt et al., *Angew. Makromol. Chem.* 132, 1 (1985).

22. U.S. Patent No. 4,332,921.

23. U.S. Patent Nos. 4,331,614 and 4,415,719.

24. Anonymous, *New Sci.* 419 (Nov. 10, 1983).

10 25. Japanese Patent Publication No. 2001-19746.

26. C.S. Wang et al., "Chemistry of Stable Brominated Epoxies", Chapter 32, in *ACS Symposium Series* 407, 1989.

27. U.S. Patent No. 5,919,844.

28. U.S. Patent No. 4,035,442.

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The flame retarding of epoxy circuit boards and, for example, other electronic epoxy applications to a V-0 standard pursuant to the UL-94 vertical test must be done with the retention of acceptable mechanical properties, for example, glass transition temperature (T_g) and with acceptable resistance to delamination. Such objectives can be attained by including in such an epoxy composition an effective amount of a composition comprising an oligomeric phosphonate comprising the repeating unit $-OP(O)(R)-O-$ Arylene- having a phosphorus content of greater than about 12%, by weight. The phosphonate species in the composition comprise those containing $-OH$ end groups as well, possibly, of those not containing $-OH$ end groups. The individual phosphonate species that contain $-OH$ end groups can be monohydroxy or dihydroxy substituted. The concentration of phosphonate species in the composition that contain hydroxy end groups will range from about 20% to about 100%, based upon the total number of termination ends ("chain ends") that potentially could hold such end groups, preferably from about 50% to about 100%. The end groups can be attached to

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the Arylene moiety or to the phosphorus moiety, and they are reactive with the epoxy functionality in the composition to which the flame retardant is added. The preferred R group is methyl, but can be lower alkyl.

5 By "Arylene" is meant any radical of a dihydric phenol. The dihydric phenol preferably should have its two hydroxy groups in non-adjacent positions. Examples include the resorcinols; hydroquinones; and bisphenols, such as bisphenol A, bisphenol F, and 4,4'-biphenol,
10 phenolphthalein, 4,4'-thiodiphenol, or 4,4'-sulfonyldiphenol. A small amount of polyhydric phenol, such as a novolac or phloroglucinol, with three or more hydroxyl groups therein can be included to increase the molecular weight.

15 The Arylene group can be 1,3-phenylene, 1,4-phenylene, or a bisphenol diradical unit, but it is preferably 1,3-phenylene.

Oligomers of this type, without indication of hydroxy end groups, are known in the art and have been described as
20 flame retardants in certain thermoplastics (as described in the prior art section at end of this document).

The oligomers of the invention can be made by any of several routes: (1) reaction of an RPOCl_2 with HO-Aryl-OH or a salt thereof, where R is lower alkyl, preferably methyl;
25 (2) reaction of diphenyl alkylphosphonate, preferably methylphosphonate, with HO-Arylene-OH under transesterification conditions; (3) reaction of an oligomeric phosphite with repeating units of the structure -
OP(OR')-O-Arylene- with an Arbuzov rearrangement catalyst,
30 where R' is lower alkyl, preferably methyl; or (4) reaction

of an oligomeric phosphite with the repeating units having the structure $\text{-OP(O-Ph)-O-Arylene}$ with trimethyl phosphite and an Arbuzov catalyst or with dimethyl methylphosphonate with, optionally, an Arbuzov catalyst-. The -OH end groups, if attached to Arylene can be produced by having a controlled molar excess of the HO-Arylene-OH in the reaction media. The -OH end groups, if acid type (P-OH), can be formed by hydrolytic reactions. It is preferred that the end groups of the oligomers be mainly -Arylene-OH types.

The amount of the phosphonate flame retardant described herein can range, in an appropriate flame retarding amount, up to about 50%, by weight of the epoxy that it is intended to flame retard, preferably from about 10% to about 30%, by weight of the epoxy resin. The additive can be employed by being cured with the epoxy (e.g., in a one-pot reaction, if desired). Alternatively, the phosphonate flame retardant can be pre-reacted with the epoxy resin in a manner analogous to what is done with tetrabromobisphenol A and epoxy (as described in U.S. Patent Nos. 6,214,468 and 6,329,474).

This invention is also useful in other epoxy formulations, including in epoxy encapsulant compositions for use in electronic applications in place of, for example, brominated flame retardants. Additionally, the compositions of this invention can also be used in structural and coating epoxy resin formulations.

If desired, the phosphonate flame retardant additive can be made, in accordance with known techniques, by utilizing a molecular weight elevating amount of a phosphate to give a more branched composition.

Also, the phosphonate compositions described herein can be used with other complementary flame retardants that are known to the person of ordinary skill in the art including, alumina trihydrate, magnesium hydroxide, ammonium
5 polyphosphate, melamine, melamine phosphate, melamine pyrophosphate, melamine polyphosphate, melamine cyanurate, red phosphorus, triphenyl phosphate, or a bisphosphate flame retardant (such as resorcinol bis(diphenyl phosphate) or bisphenol A bis(diphenyl phosphate)).

10 The epoxy resin of this invention can contain other components conventionally used, such as polyphenylene oxide, imide, phenolic, and bisoxazine resins.

The following Examples, which should not be construed in a limiting fashion, further illustrate the invention.

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Example 1

In this run, 124 g (0.5 mol) of diphenyl methyl-
5 phosphonate, 113 g (1.03 mol) of resorcinol and 0.54 g of
sodium methylate were heated and stirred in a reaction
flask at 230°C. The reaction flask was provided with an
about 40 cm-high Vigreux column wrapped with electrical
heating tape and insulation to keep the phenol and any
10 volatilized resorcinol from solidifying in the column.
Vacuum was gradually dropped from 625mm to 5 mm Hg. The
reaction stopped after four hours. Phenol was distilled
off during reaction, and 93 g of distillate (about 1 mol
if calculated as phenol) was collected in the cold trap
15 with 241 g remaining in the reaction flask. The
distillate appeared to be almost pure phenol.

Characterization: The sample was a coffee-colored
dark, but transparent, viscous liquid. It was pourable
when warm and was soluble in 2-butanone and DMSO.
20 Titration by tetrabutylammonium hydroxide to azo violet
end point indicated an equivalent weight of 158 per OH
group. Assuming there are two OH end group, then the
molecular weight will be $158 \times 2 = 316$. The theoretical
value was 280, indicating oligomer formation of a very low
25 polymerization degree. The ^{31}P NMR spectrum showed a
series of peaks between 25.7 and 27.5 ppm. These data
support a structure that is mainly of the structure
 $\text{CH}_3\text{P}(=\text{O})(\text{OC}_6\text{H}_4\text{OH})_2$ with some of the structure
 $\text{HOC}_6\text{H}_4\text{OP}(=\text{O})(\text{CH}_3)\text{OC}_6\text{H}_4\text{OP}(=\text{O})(\text{CH}_3)\text{OC}_6\text{H}_4\text{OH}$ and only a small
30 percentage of remaining phenoxy groups.

Example 2

In this synthesis, 200 g (0.8 mol) of diphenyl methylphosphonate (DPMP), 89 g (0.8 mol) of resorcinol and
5 0.43 g of sodium methylate were reacted at 245°C. The temperature was gradually raised to 260°C over the course of three and one half hours. During the reaction 141 g of condensate was collected in the trap and was found to be almost pure phenol, evidenced by the infrared spectrum.
10 This suggests that 94% of the phenoxy groups in DPMP had been displaced by resorcinol. About 136 g of product remained in the reaction flask. The final product was a clear light amber glassy solid.

Characterization: The sample was soluble in acetone,
15 methanol, chloroform and 2-butanone. Its infrared spectrum showed a small peak in the region of -OH group absorption.

The ^1H NMR showed chemical shifts for PCH_3 (d, 3 protons, 1.77ppm, CDCl_3) and Ar-H (m, 4 protons, 7.0-
20 7.4). A reasonable structure fitting this data is an oligomer with the repeating unit $-\text{OP}(=\text{O})(\text{CH}_3)\text{OC}_6\text{H}_4-$ with HOC_6H_4- and some C_6H_5- end groups.

Example 3

In this synthesis, 170 g (0.69 mol) of diphenyl methyl-phosphonate, 72 g (0.65 mol), 0.20 g (0.61×10^{-3} mol) of triphenyl phosphate, and 0.025 g of sodium methylate were heated at 240 C for six and one half hours. Vacuum applied to remove phenol was gradually dropped from 625 mm to 0.3 mm Hg and, at the same time, the temperature was gradually raised to 260°C over the course of five hours. About 137 g of phenol was collected in the trap, whereas 103 g of product remained in the reaction flask. The final product was a clear light yellow solid, which was pourable at 80°C.

Characterization: The product was soluble in acetone, 2-butanone and DMF. Titration in DMF solution by tetrabutylammonium hydroxide gave an equivalent weight for OH end groups of about 650.

Example 4

To a three-necked flask equipped with thermometer, magnetic stirrer, distillation head and nitrogen inlet 163 g
5 (0.52 mol) of triphenyl phosphite and 1.0 mL of methyl iodide were charged. Then, 32.7 g (0.26 mol) of trimethyl phosphite was added drop-wise at 100-110°C over the course of one hour. The reaction temperature was then raised to 210°C and an exothermic reaction was observed. The reaction
10 temperature was maintained at 230°C for two hours, and the reaction mixture was analyzed before it underwent transesterification. Diphenyl methylphosphonate was obtained as a liquid. The ^{31}P NMR (CDCl_3) indicated 95% diphenyl methylphosphonate. The impurities included
15 triphenyl phosphate (0.8%, $\delta = -16.4\text{ppm}$), trimethyl phosphate (0.6%, $\delta = -10.3\text{ppm}$), and unknown compounds ($\delta = 19.8, 20.4, 28.4\text{ppm}$). The acid number of this crude diphenyl methylphosphonate was 5.4 mg KOH/g

Then, 86 g (0.78 mol) of resorcinol and 0.024 g ($4.4 \times 10^{-4}\text{mol}$) of sodium methoxide was charged to the above-
20 described reaction mixture. The resulting transesterification reaction was performed at 215°C to 230°C for eighteen hours. Vacuum was applied after four hours to remove the phenol. Phenol was collected (130 g), whereas
25 148 g of product remained in the reaction flask. This final product, was a dark reddish solid, which was pourable when heated above 100°C.

Characterization: Titration of the sample with tetrabutyl-ammonium hydroxide gave an equivalent weight of 978 to the
30 end point determined by either azo violet indicator or the

potentiometric method. The ^{31}P NMR showed multiple peaks between δ 25 and 31ppm, and ^1H NMR suggested several kinds of methylphosphonate structures in the final product.

Example 5

To a three-necked flask equipped with thermometer, magnetic stirrer, distillation head and nitrogen inlet was charged 148 g (0.48 mol) of triphenyl phosphite, 0.9 mL of methyl iodide and 31 g (0.25 mol) of dimethyl methylphosphonate at 110°C. The reaction temperature was gradually raised. At 210°C a rapid exothermic reaction lasting about fifteen minutes was observed. The reaction mixture was stirred further for one hour at 230°C. The crude diphenyl methylphosphonate was a colorless transparent liquid mixture. The ^{31}P NMR (CDCl_3) showed 93% diphenyl methylphosphonate. The impurities included triphenyl phosphate (0.3%, $\delta = -16.4\text{ppm}$) and unknown compounds ($\delta = 19.8$ (2.8%), 20.4 (2.8%), 28.4 (1.0%)ppm). The acid number of this crude diphenyl methylphosphonate was 8.1 mg KOH/g.

Then, 80 g (0.73 mol) of resorcinol and 0.040 g (7.4×10^{-4} mol) of sodium methoxide was charged to the above-described reaction mixture. The transesterification reaction was performed at 205°C to 230°C for eighteen hours. Vacuum was applied after four hours to remove the phenol, and 130 g of phenol was collected. About 120 g of product remained in the reaction flask.

The product was a transparent yellowish viscous solid, which was pourable above 100°C. Titration by tetrabutylammonium to the end point determined by either azo violet indicator or the potentiometric method hydroxide gave an equivalent OH weight of 3000. The ^{31}P NMR of the sample showed small

multiple peaks between δ 25 and 31 ppm, and ^1H NMR suggested mainly three kinds of methylphosphonate structures.

Example 6

In this run, 146.8 g (0.59 mol) of purified diphenyl methylphosphonate, 65.41 g (0.59 mol) of hydroquinone and 0.17 g of sodium methylate were reacted at 225°C for ten and one half hours. The reactor was provided with an about 40 cm-high Vigreux column wrapped with electrical heating tape and insulation to keep the phenol and any volatilized resorcinol from solidifying in the column. Vacuum was applied to remove phenol from the reaction mixture, and it gradually dropped after two hours from 625mm to 5 mmHg. About 106 g of material was collected in the trap and was found to be almost pure phenol, as evidenced by its NMR spectrum. About 105 g of material remained in the reaction flask. The final product was a clear light amber-yellow glassy solid, which was pourable above 90°C.

Characterization: The potentiometric titration of the sample by tetrabutylammonium hydroxide in DMF solution gave an equivalent OH weight of 9200. Its acid number by alcoholic KOH titration to p-naptholbenzein end point was 9.70mg KOH/g.

Example 7 (Evaluation in Epoxy Resins)

Preparation of laminates: The fire retardant additives from Examples 1 - 6 and epoxy was dissolved in 30 % of 2-butanone at 60 C. Then, 1 wt% of 2-methyl imidazole (AMI-2 brand, from Air Products) was added. The resultant warm varnish was applied to a glass fiber mat (7628, BGF, 0.17 mm). The prepreg was dried at room temperature overnight and then at 90°C for thirty minutes. A nontacky, transparent prepreg was obtained. Eight layers of the prepreg were stacked, sided with copper foil (0.035 mm thick), precured for thirty minutes at 130°C and 8 MPa pressure and then cured for sixty minutes at 171 C and 30 MPa pressure.

Test Procedure: The flammability of the prepregs was measured by the standard UL 94-tests (vertical protocol). The glass transition temperature was measured by TMA according to the IPC TM-650 2.4.24 standard. The time to delamination was measured by TMA at 260°C according to the IPC TM-650 2.4.24.1 standard.

The results of these tests are shown in Table 1, which follows.

Table 1. Flammability and thermal properties of laminates

	7-1	7-2	7-3	7-4	7-5	7-6	7-7	7-8	7-9	7-10	7-11
Epoxy 1 ^a	69			69							
Epoxy 2 ^b		69			69	74	79				69
Epoxy 3 ^c			69					69	69	69	
Product Ex. 1	30	30	30								
Product Ex. 2				30	30	25	20				
Product Ex. 3								30			
Product Ex. 4									30		
Product Ex. 5										30	
Product Ex. 6											30
Catalyst AMI-2	1	1	1	1	1	1	1	1	1	1	1
UL 94	V-1	V-0	V-1	V-1	V-0	V-0	V-0	V-0	V-0	V-0	V-0
T _g , °C	110	135	135	130	160	190	135	163	140	157	140
Delamination, 260 °C	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail

^a Bisphenol A epoxy resin^b Phenol-novolac epoxy resin.^c Cresol-novolac epoxy resin.

We Claim:

1. A composition comprising a hydroxy-terminated oligomeric phosphonate comprising the repeating structure
5 -OP(=O)(R)OArylene-, where R is alkyl.

2. A composition as claimed in Claim 1 wherein the content of hydroxy-terminated phosphonate ranges from about 20% to about 100%, based upon the total number of termination ends that
10 potentially could hold such end groups, preferably from about 50% to about 100%.

3. A composition as claimed in Claim 1 wherein Arylene is 1,3-phenylene.
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4. A composition as claimed in Claim 1 wherein R is lower alkyl.

5. A composition as claimed in Claim 1 wherein Arylene is 1,3-phenylene and R is lower alkyl.
20

6. A composition as claimed in Claim 1 wherein Arylene is 1,3-phenylene and R is methyl.

7. A composition as claimed in Claim 1 wherein Arylene is a bisphenol diradical unit.
25

8. A composition as claimed in Claim 1 wherein Arylene is a bisphenol diradical unit and R is methyl.
30

9. A thermoset resin composition comprising a phosphonate as claimed in any of Claims 1-8, optionally in the presence of another flame retardant.

5 10. An epoxy resin composition containing a phosphonate as claimed in any of Claims 1-8, optionally wherein the phosphonate and the epoxy have been prereacted with one another, optionally in the presence of another flame retardant.

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11. An epoxy laminate meeting a flame retardant UL-94 rating of V-0 and resistant to delamination which comprises a flame retarding amount of an oligomeric hydroxy-terminated phosphonate as claimed in any of Claims 1-8, optionally in the
15 presence of another flame retardant.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F9/40 C08L63/00 C08G59/40 C08G79/04 C08L85/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL ABSTRACTS, vol. 81, no. 22, 2 December 1974 (1974-12-02) Columbus, Ohio, US; abstract no. 137482, ORITO, ZENICHI ET AL: "Fire-resistant polyesters moldings" XP002227623 abstract & JP 49 005454 A (MITSUBISHI RAYON CO., LTD.) 18 January 1974 (1974-01-18)	1-11
Y	GB 1 308 521 A (ESSO RESEARCH AND ENGINEERING CO.) 21 February 1973 (1973-02-21) the whole document	1-11

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FR 2 348 197 A (CIBA-GEIGY AG) 10 November 1977 (1977-11-10) the whole document ----	1-11
Y	FR 1 438 381 A (GELSENBERG BENZIN AG) 13 May 1966 (1966-05-13) the whole document ----	1-11
Y	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 16, 8 May 2001 (2001-05-08) & JP 2001 019746 A (ASAHI DENKA KOGYO KK), 23 January 2001 (2001-01-23) cited in the application abstract ----	1-11
Y	DE 31 39 958 A (BASF AG) 28 April 1983 (1983-04-28) cited in the application the whole document ----	1-11
Y	US 2 716 101 A (HARRY W. COOVER) 23 August 1955 (1955-08-23) cited in the application the whole document ----	1-11
Y	US 2 682 522 A (HARRY W. COOVER) 29 June 1954 (1954-06-29) cited in the application the whole document -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 02/31917

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 49005454	A	18-01-1974	NONE	
GB 1308521	A	21-02-1973	NONE	
FR 2348197	A	10-11-1977	BE 853520 A1	13-10-1977
			DE 2715589 A1	27-10-1977
			FR 2348197 A1	10-11-1977
			GB 1540504 A	14-02-1979
			JP 52128359 A	27-10-1977
			NL 7704042 A	18-10-1977
			US 4196119 A	01-04-1980
			US 4246170 A	20-01-1981
			US 4148820 A	10-04-1979
FR 1438381	A	13-05-1966	DE 1194414 B	10-06-1965
			AT 248458 B	25-07-1966
			BE 659633 A	
			CH 449008 A	31-12-1967
			NL 6503926 A	29-09-1965
JP 2001019746	A	23-01-2001	NONE	
DE 3139958	A	28-04-1983	DE 3139958 A1	28-04-1983
US 2716101	A	23-08-1955	NONE	
US 2682522	A	29-06-1954	NONE	

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